Microstructural study of SiO_2 doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites

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in
Ceramic Engineering

By

Pragyan Parmita Das

Roll No-**110CR0603**

Under the Guidance of
Prof. Bibhuti B. Nayak

Department of Ceramic Engineering
National Institute of Technology
Rourkela
2014

Certificate

This is to certify that the thesis entitled, "Microstructural study of SiO_2 doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites" submitted by Ms. Pragyan Parmita Das in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date: 14/5/14

Prof. Bibhuti B. Nayak
Dept. of Ceramic Engineering
National Institute of Technology
Rourkela - 769008

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Pragyan Parmita Das
14/5/2014

Pragyan Parmita Das

Roll No: 110CR0603
Department Of Ceramic Engineering
NIT, Rourkela

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ABSTRACT

In this project, 3 mol % Y_2O_3 stabilized ZrO_2 and mixture of 3 mol % Y_2O_3 and Al_2O_3 stabilized ZrO_2 have been prepared via precipitation route using hydrazine hydrate. The as-synthesized powders were pelletized and sintered at 1200°C for 2h. Phase pure t-ZrO_2 was obtained for 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 sintered pellet. To study the microstructural development of this composite material, two different weight of 0.05g and 0.1g of fumed SiO_2 powders were mixed thoroughly with the calcined (600°C) 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 powders. All these mixed powders were pelletized and sintered at 1200°C, 1300°C, 1400°C and 1500°C for 2h. AP, BD was calculated for these sintered composite materials. XRD was performed using Cu-K_α radiation on these powders. FE-SEM was performed to study the microstructure of these composite materials. It was found that addition of SiO_2 modify the microstructure of 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites and may be possible for dental application.

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CHAPTER 1

INTRODUCTION

1.1 Introduction:

Zirconia (ZrO_2) is used as a structural ceramic materials due to its physical and chemical properties, including hardness, wear resistance, low coefficient of friction, elastic modulus, chemical inertness, ionic conductivity, electrical properties, low thermal conductivity, and high melting temperature [1-3].

Bulk ZrO_2 exhibits cubic (c) fluorite structure, tetragonal (t) structure and monoclinic (m) structure. Pure ZrO_2 has monoclinic structure at room temperature and undergoes m→ t and t→ c phase transitions at 1173°C and 2370°C respectively. It has been found that the high temperature ZrO_2 forms can be stabilized at room temperature by addition of a small amount of oxides as MgO, CaO, Y_2O_3, CeO_2 etc [2-5]. When small percentages of the above said dopant is being added, the phase changes and the resulting material with 't' or 'c' crystal structure, shows excellent mechanical properties. Doped zirconia in tetragonal phase in case of tetragonal zirconia polycrystals (TZP), shows better mechanical properties and this material could be useful for dental applications by modifying the microstructure.

Different concentrations of secondary phase such as Al_2O_3 or SiO_2 or Y_2O_3 doped zirconia is very widely used for dental applications. Secondary phase doped 3Y-TZP (3 mol% Y_2O_3 stabilized ZrO_2) with suitable microstructure could be possible by different wet-chemical synthesis route. For dental applications it was fabricated with the microstructure which contains small grains, which depend upon the sintering temperature. Doped partially stabilised tetragonal zirconia (Y-TZP) has become popular with an alternative restorative in dentistry field [6]. In this project, SiO_2 doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites have been prepared and microstructural study was performed in detail, so that this material could be useful for dental applications.

1.2 Objectives:

To study the structure and microstructure of SiO_2 doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites materials for suitability in dental industry.

To achieve this objective, precipitation route was followed to prepare 3 mol % Y_2O_3 stabilized ZrO_2 and mixture of 3 mol % Y_2O_3 and Al_2O_3 stabilized ZrO_2.

To study the microstructural development of this composite material, two different weight of 0.05g and 0.1g of fumed SiO_2 powders were mixed thoroughly with 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 powders.

All these mixed powders were pelletized and sintered at 1200°C, 1300°C, 1400°C and 1500°C for 2h.

Apparent porosity, Bulk density, Structure, microstructural study was performed and results are analysed.

CHAPTER 2:

LITERATURE REVIEW

2.1 Introduction:

Zirconia based composite materials having 3 mol % of Yitria(Y_2O_3) as a stabilizer is used for biomedical applications [6-8]. 3Y-TZP has always been used for the fabrication in dental ceramics as dental crowns and fixed partial dentures. The reformations is processed used here is either by soft machining or sintering it at a very high temperature. Various wear free procedures is developed to obtain dentals crowns an bridges which is used to increase the strength and reliability in dental applications. As 3Y-TZP has good fracture toughness it is highly resistance to crack propagation and catastrophic fracture. The ceramic material of 3Y-TZP is used in the dental application, due to its high degree of opacity and translucency and biocompatibility [8-12]. It has been found that by introducing a compressive surface tension it increases the flexural strength and also its resistivity towards ageing [13-17]. It was also found that the opaque optical behaviour can be estimated by the fact that it should be increase in grain size, with increase in high refractive index, decrease in absorption coefficient [11-17].

2.2 Synthesis of 3Y-TZP Powder doped with Al_2O_3:

Various methods such as low temperature sintering, colloidal technique, spray pyrolysis and sol gel combustion are used to produce the composites of 3Y-TZP with alumina ,but the above methods have a high amount of production cost .Therefore co-precipitation method is widely accepted for the production to provide a better quality products with minimum cost of production .This methods provides fine and uniformly distributed mixture for the synthesis of 3Y-TZP particles. It has been found that the little amount Y_2O_3 in alumina (Al_2O_3) also enhances densification process [18] and Al_2O_3 doped zirconia also improve the mechanical properties [19, 20]. It has been found that when alumina (Al_2O_3) was added to tetragonal zirconia polycrystal its mechanical properties enhances [19, 20].

2.3 Microstructural study of silica doped in Zirconia:

The composites in the presence of silica improve the stiffness, flexural strength and fatigue resistance. Silica was found in the triple junction but not in the grain boundaries or lattices. Undoped zirconia always have a separate grains and very important is the internal stress doped zirconia always shows a rounded structure than the un-doped one the silica here is used to create a glassy phase along the grain boundaries and also help in densification preventing the propagation of various cracks. In the lower temperature the presence of glassy phase increase the mechanical properties and improves the densification of high temperature material to liquid phase, it show better sintering conditions [21,22]. It was found that doping with silica is very much advantageous in improving their super plasticity of TZP and has maximum elongation of about 1000%. It was found that the fracture strain increases for a samples of about greater than 1% of SiO_2.

CHAPTER 3

EXPERIMENTAL

3.1 Synthesis of 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites

3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites were prepared using co-precipitation route using hydrazine hydrate and schematic flow diagram for processing of this composite material is shown in Fig. 3.1.

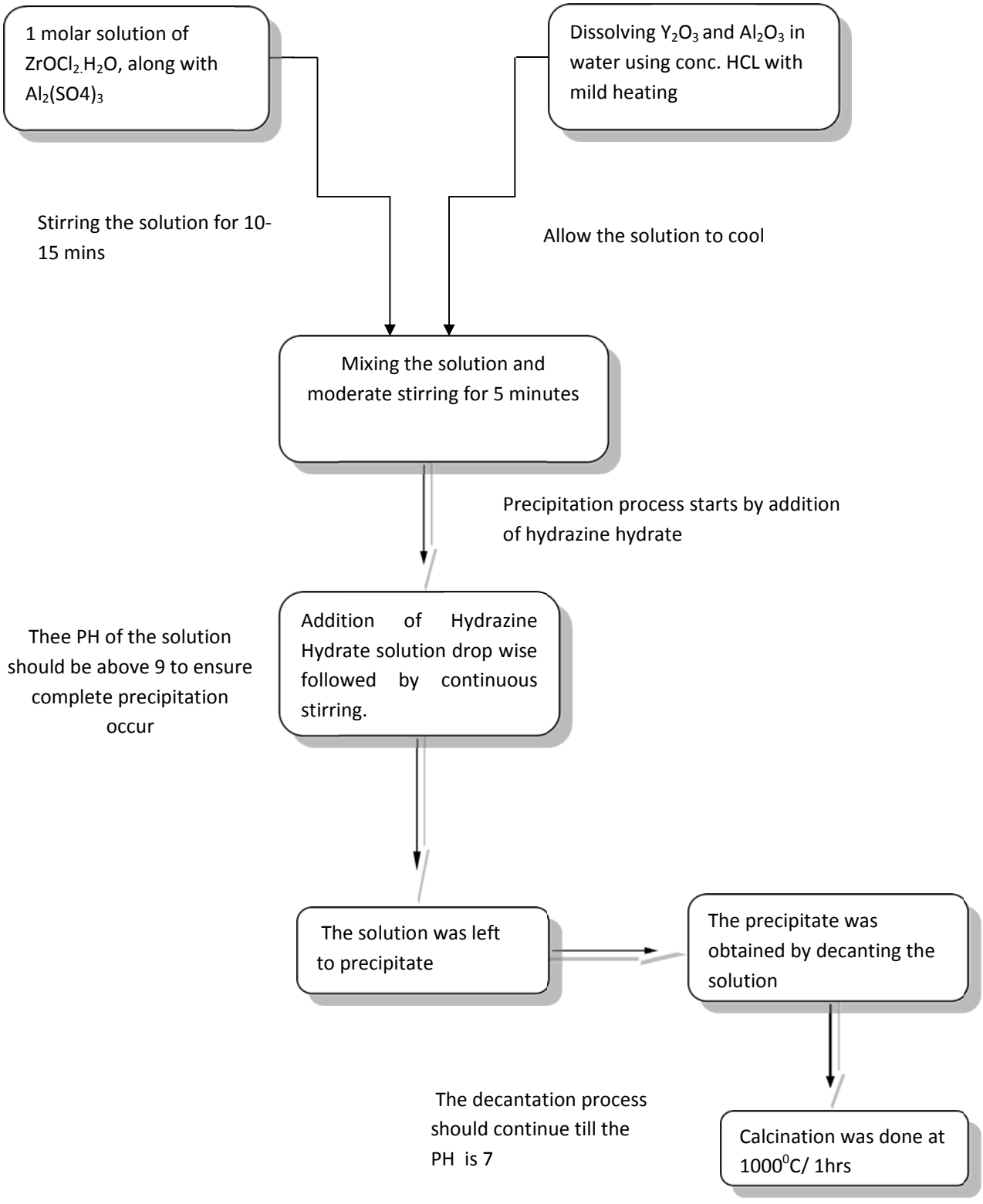


Fig. 3.1: Synthesis of 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites

Batch Calculation:

1 mol of $ZrOCl_2.8H_2O$ = 12.042 g

1mol of Y_2O_3 = 0.2681 g

1mol of $Al_2(SO_4)_3$ = 0.336 g

1mol of $(ZrO_2)_{0.94}$ $[(Y_2O_3)_{0.03}$ $(Al_2O_3)_{0.03}]$ =124.43076 g

(a**) For Y_2O_3:**

124.43076 g contains 6.7743 g of Y_2O_3

5 g will contains 0.2722 g of Y_2O_3

(b**) For $ZrOCl_2.8H_2O$:**

124.43076 g contains 114.59646 g of ZrO_2

5 g contains 4.6048 g of ZrO_2

1mol of ZrO_2 =1 mol of $ZrOCl_2.8H_2O$

Amount of $ZrOCl_2.8H_2O$ required for 0.03737 mole of ZrO_2 = 12.024 g

(c**) For Al_2O_3:**

124.43076 g contains 3.06 g of Al_2O_3

5g contains 0.1229 g of Al_2O_3

(d) **For $Al_2(SO4)_3$**:

1mol of Al_2O_3 = 1mol of $Al_2(SO_4)_3$

0.00120 mol of Al_2O_3 = 0.3336 g

The calcined (650°C) 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 powders were mixed with fume SiO_2 at two different weights such as 0.05 g and 0.1 g. The composites of SiO_2 doped powders were pelletized using polyvinyl alcohol (PVA 3%). The pellets of respective compositions were sintered at 1200^0C, 13000C, 14000C and 1500^0C respectively with a soaking time of 2 h.

3.2 Characterization:

3.3 Bulk Density and Porosity:

The bulk density of sintered pellets was calculated by calculating their dry weight, soaked weight and suspended weight after placing the pellets within the vaccum or dessicator for time interval of 1hours which is dipped inside a kerosene sample as it is non-reactive after removing the air, the samples suspended weight was calculated followed by soaked weight by wiping it with a bit tissue paper. So by using the Archimedes Principle the bulk density of the sample was calculated by the following way:

Bulk Density (B.D)= D/W-S
Where,
D= Dry weight
W=soaked weight
S=suspended weight

Apparent Porosity (A.P) = (Soaked weight – Dry Weight) / (Soaked weight –Suspended Weight)*100

3.4 Microstructure:

FE-SEM analysis was carried out for the samples to analyse the grain morphology or grain boundaries structure of various samples in field emission scanning electron microscope (FESEM). The pellets are then coated with Au and microstructural analysis was performed.

3.5 XRD Analysis of different samples

Phase analysis was studied using the room temperature powder X-ray diffraction (Rigaku) with filtered 0.154056 nm Cu Kα radiation.

CHAPTER 4:

RESULTS AND DISCUSSION

4.1 Analysis of Bulk Density:

The pelletized samples of 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 doped with 0.05 gm of SiO_2 was sintered at different temperatures ranging from 1200^0C to 1500^0C and the change in bulk density of different samples as a function of sintering temperatures is shown in the Figure 4.1 (a). The bulk density increases with temperature and it may be due to decrease of porosity and better microstructure.

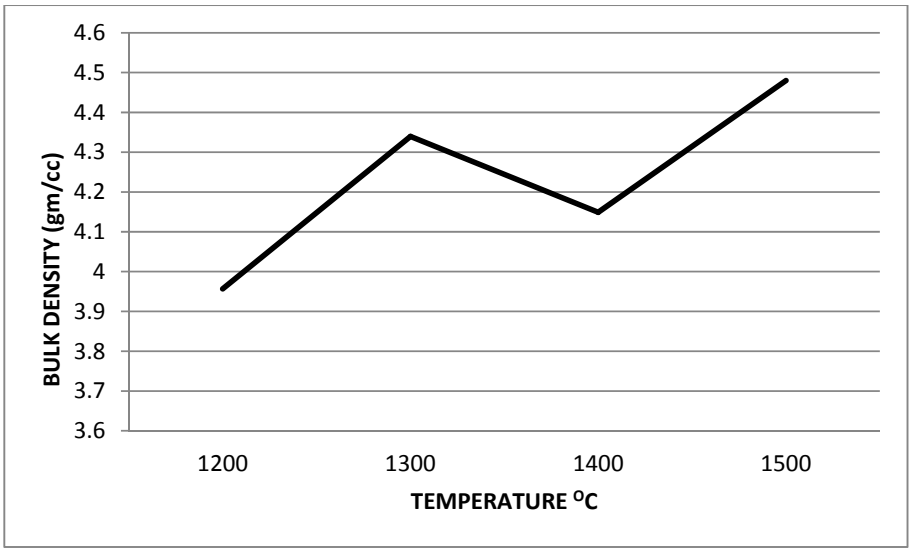


Fig. 4. 1(a): Bulk density as a function of sintering temperature of 0.05g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites

The pelletized samples of 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 doped with 0.1 gm of SiO_2 was sintered at different temperatures ranging from 1200^0C to 1500^0C and the change in bulk density of different samples as a function of sintering temperatures is shown in the Figure 4.1 (b). The bulk density increases and nearly constant from 1300°C to 1500°C and it may be due to decrease of porosity and better microstructure.

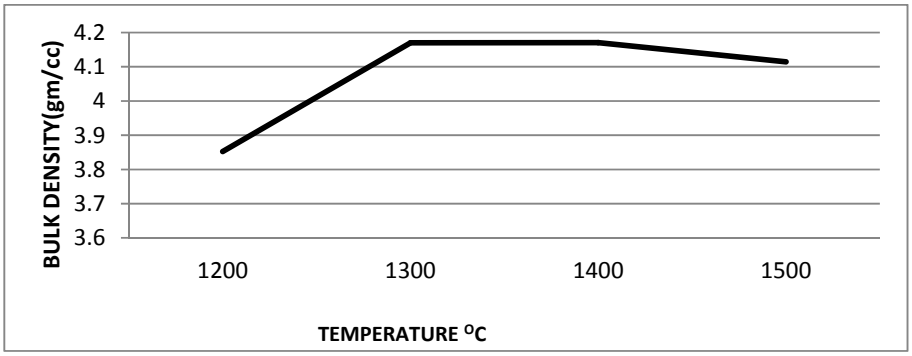


Fig. 4. 1(b): Bulk density as a function of sintering temperature of 0.1g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites

4.2 Analysis of Apparent Porosity:

The pelletized samples of 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 doped with 0.05 gm of SiO_2 was sintered at different temperatures ranging from 1200^0C to 1500^0C and the change in apparent porosity of different samples as a function of sintering temperatures is shown in the Figure 4.2 (a). The apparent porosity decreases continuously from 1200°C to 1500°C and it was co-related with bulk density results of this sample.

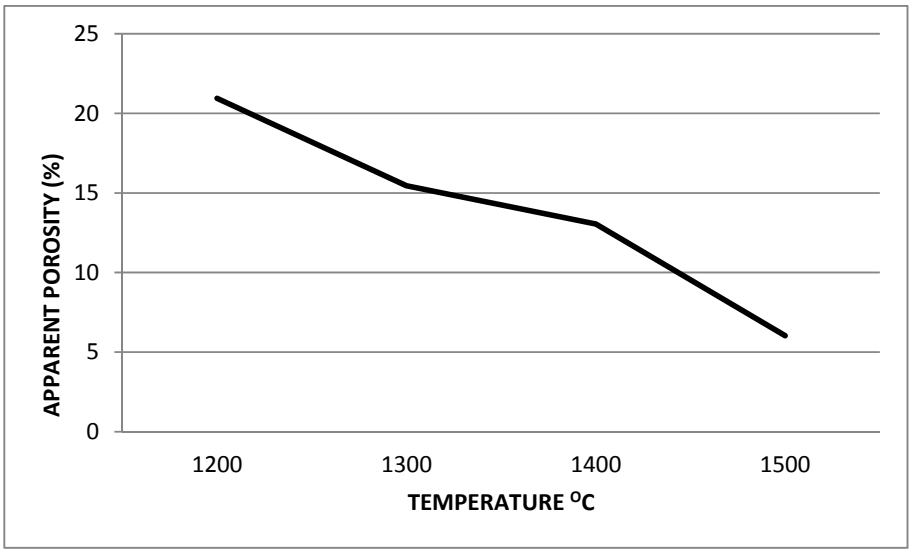


Fig. 4. 2(a): Apparent porosity as a function of sintering temperature of 0.05g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites

The pelletized samples of 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 doped with 0.05 gm of SiO_2 was sintered at different temperatures ranging from 1200^0C to 1500^0C and the change in apparent porosity of different samples as a function of sintering temperatures is shown in the Figure 4.2 (b). The apparent porosity decreases continuously, but nearly constant from 1300°C to 1500°C and it was co-related with bulk density results of this sample.

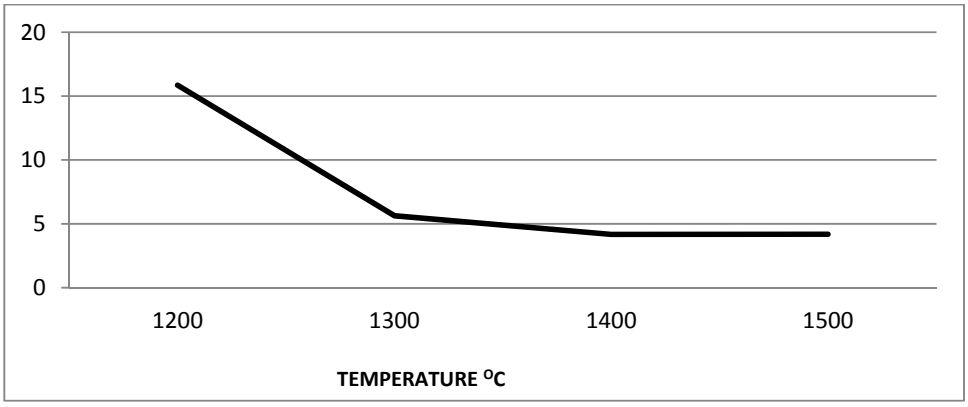
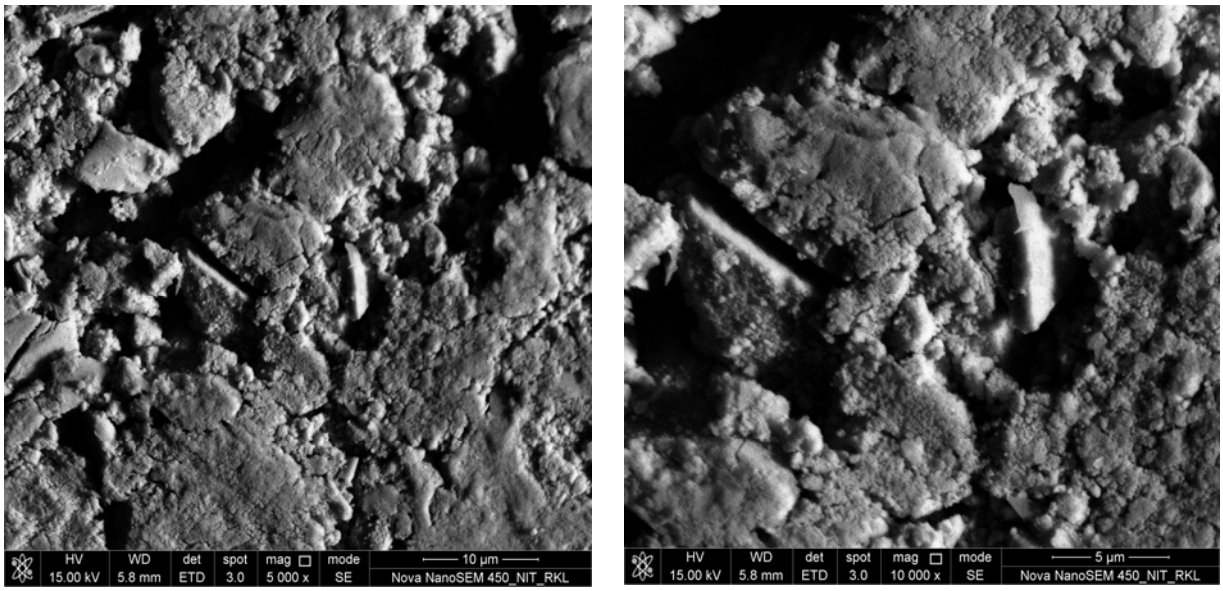


Fig. 4. 2(b): Apparent porosity as a function of sintering temperature of 0.1g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites

4.3 Microstructure:

The microstructural analysis was done for sintered 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.3 shows FE-SEM micrographs of sintered (1200°C) 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has pores and it is not fully dense.



. Fig. 4. 3: FE-SEM micrographs of sintered (1200°C) 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.4 shows FE-SEM micrographs of sintered (1200°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has similar morphology with that of the parent sample (3 mol % (Y_2O_3+Al_2O_3): ZrO_2).

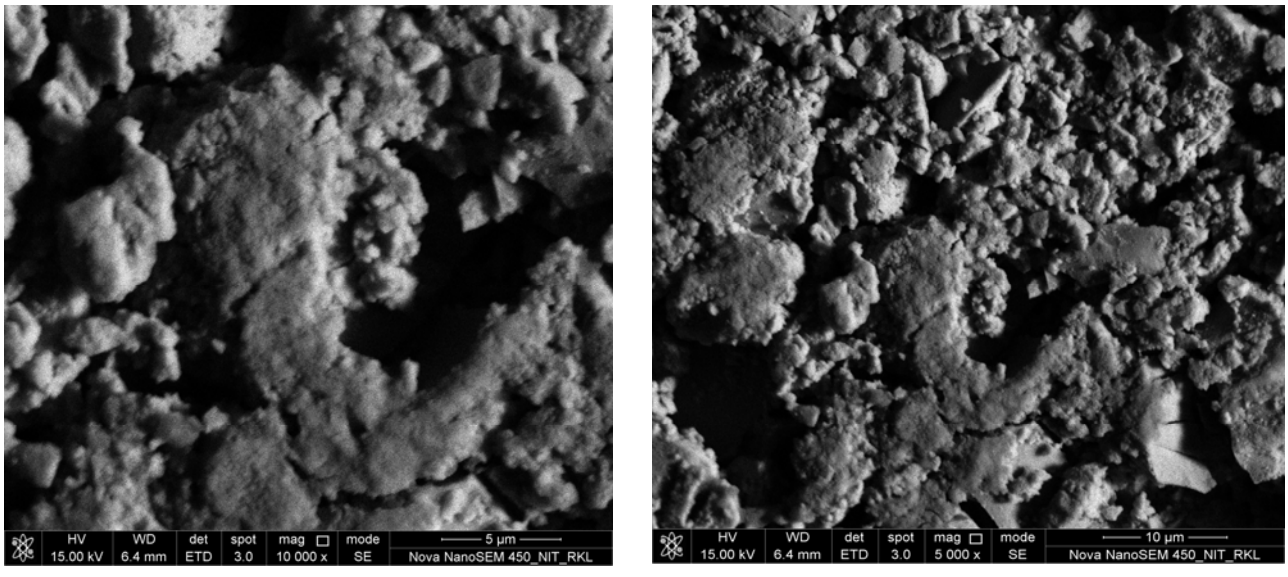


Fig. 4. 4: FE-SEM micrographs of sintered (1200°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.5 shows FE-SEM micrographs of sintered (1200°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has pores but relatively smaller than that of the parent sample (3 mol % (Y_2O_3+Al_2O_3): ZrO_2). This sample is showing better microstructure as compared to 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples.

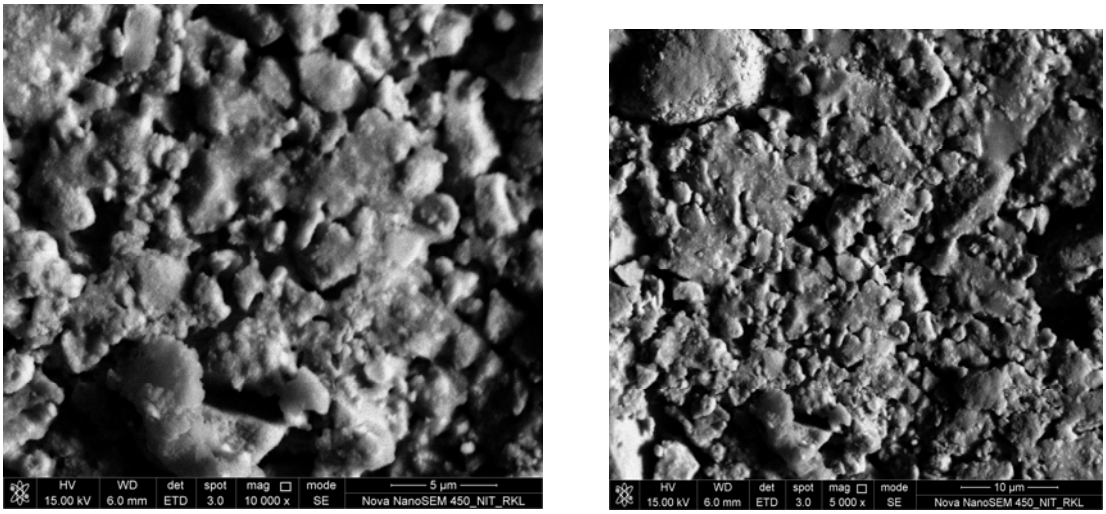


Fig. 4. 5: FE-SEM micrographs of sintered (1200°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.6 shows FE-SEM micrographs of sintered (1300°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has better micrograph as compared with 1200°C sintered samples. Phase segregation was observed in this sample sintered at 1300°C. This sample is showing better density with lower content of porosity.

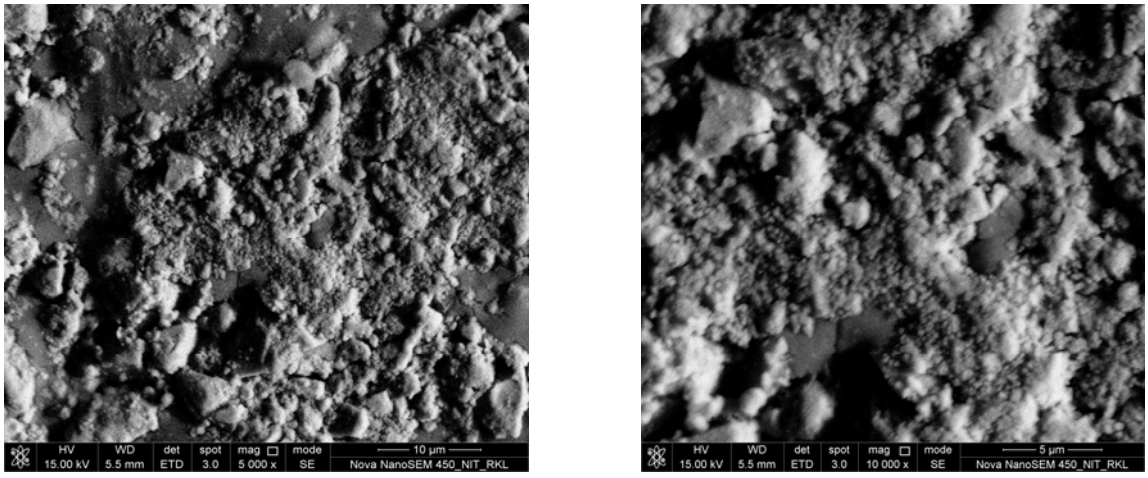


Fig. 4. 6: FE-SEM micrographs of sintered (1300°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.7 shows FE-SEM micrographs of sintered (1300°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has better micrograph as compared with 1200°C sintered samples. Phase segregation was observed in this sample sintered at 1300°C. This sample is showing better density with lower content of porosity.

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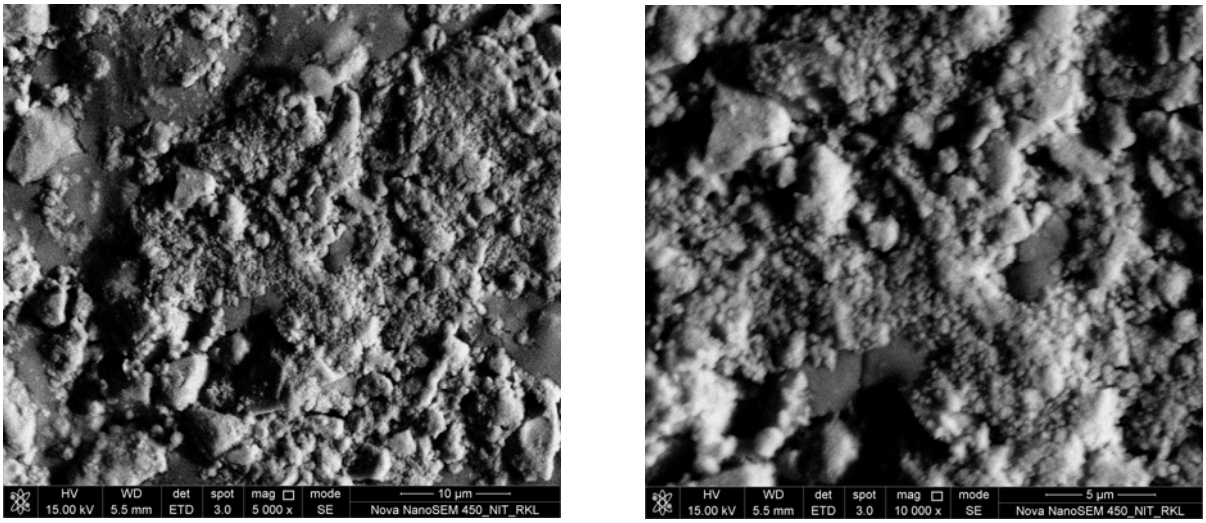

Fig. 4. 7: FE-SEM micrographs of sintered (1300°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.8 shows FE-SEM micrographs of sintered (1400°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has better micrograph as compared with 1200°C sintered samples.

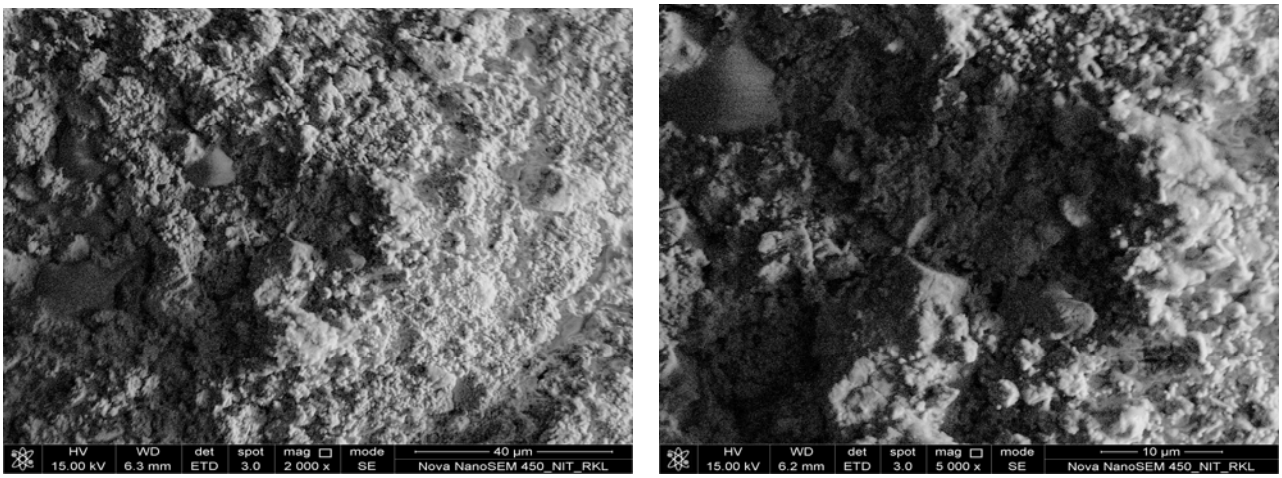

Fig. 4. 8: FE-SEM micrographs of sintered (1400°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.9 shows FE-SEM micrographs of sintered (1400°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has better micrograph as compared with 1200°C sintered samples. The micrographs also suggest that the densification along the grains has occurred and the grains are nearly in spherical in nature.

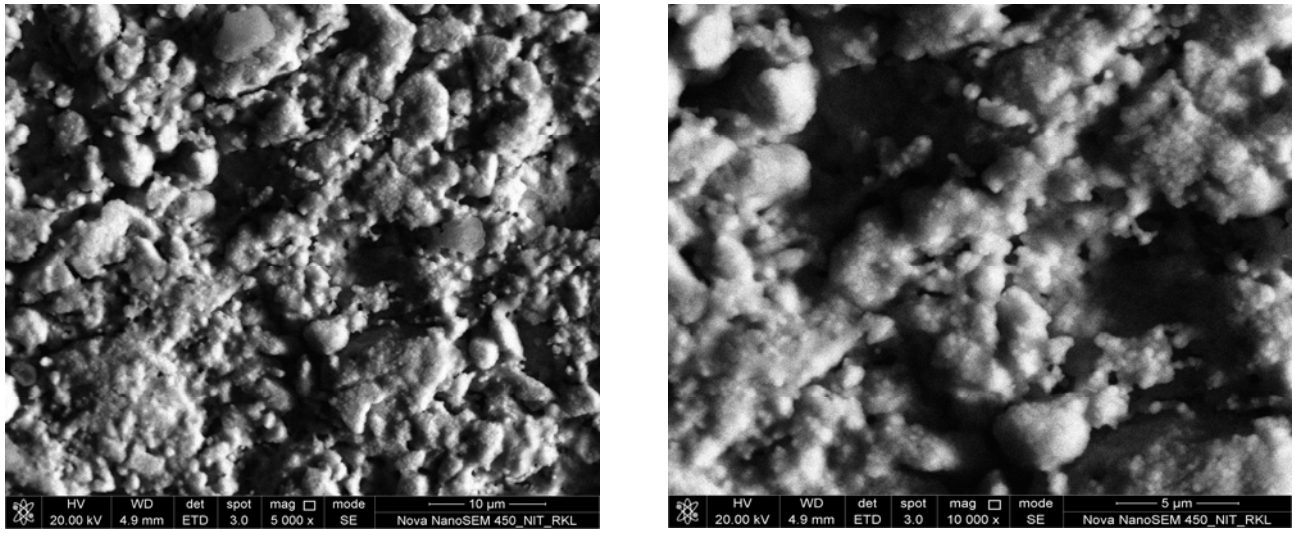

Fig. 4. 9: FE-SEM micrographs of sintered (1400°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.10 shows FE-SEM micrographs of sintered (1500°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has better micrograph as compared with other sintered samples. At this temperature very good densification has occurs along the grain boundaries and the grain show uniaxial shapes.

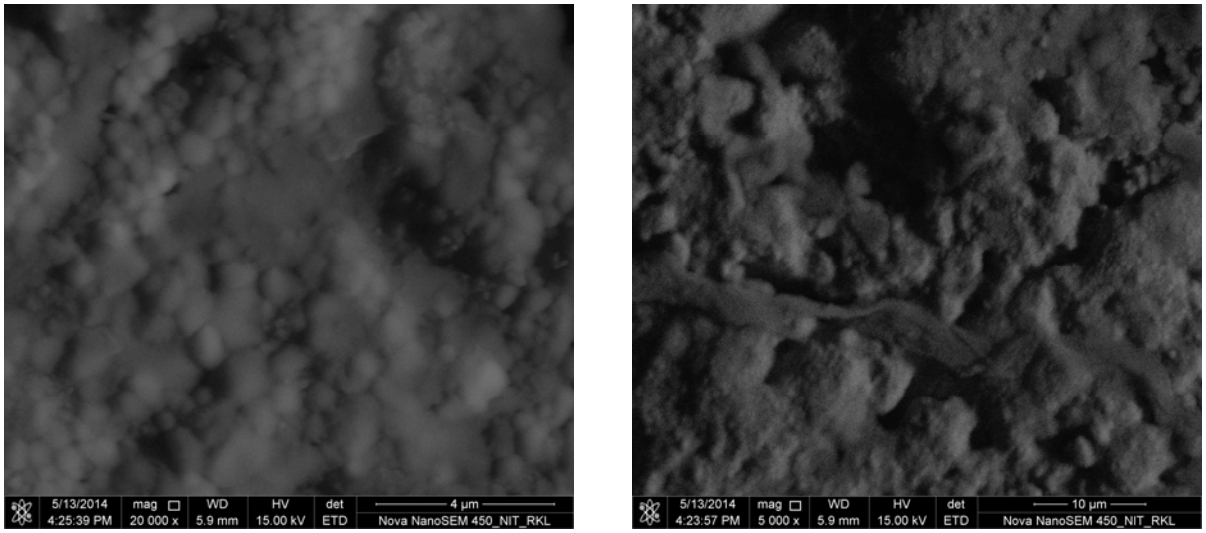

Fig. 4. 10: FE-SEM micrographs of sintered (1500°C) 0.05 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

The microstructural analysis was done for sintered 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. Fig. 4.11 shows FE-SEM micrographs of sintered (1500°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 samples. The two different magnified micrographs indicate that the sample has better micrograph as compared with other sintered samples. At this temperature very good densification has occurs and this sample is showing better microstructure than other prepared samples.

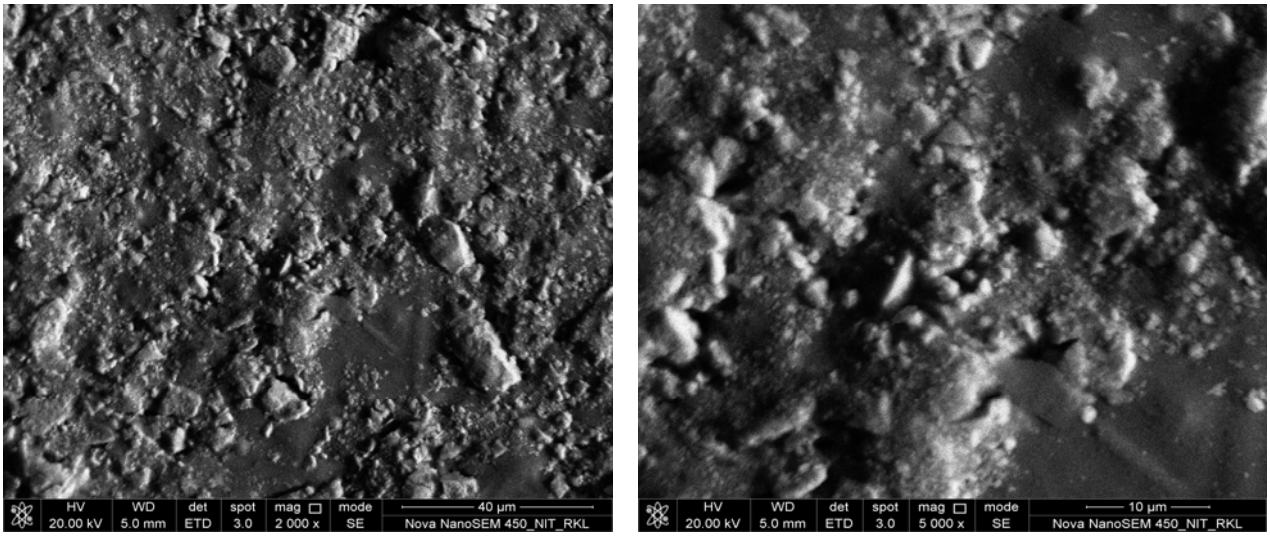

Fig. 4. 11: FE-SEM micrographs of sintered (1500°C) 0.1 g SiO_2 doped 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 composites.

4.4 Structure

X ray diffraction pattern of 3 mol % (Y_2O_3): ZrO_2 composite sinterted at 1200°C is shown in Fig. 4.12. All the peaks are matched with t-ZrO_2 phase with small amount of m-ZrO_2 phase.

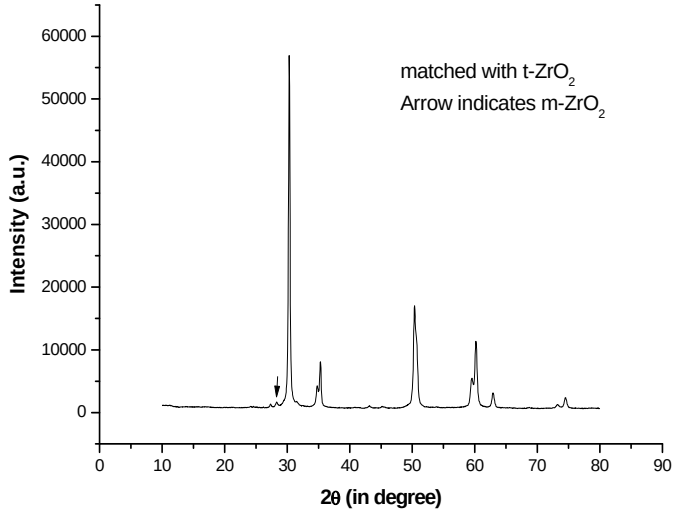

Fig. 4. 12: XRD pattern of sintered (1200°C) 0 3 mol % (Y_2O_3): ZrO_2 composites

Structural analysis was performed using XRD for 3 mol % Al_2O_3 doped 3 mol % (Y_2O_3): ZrO_2 sample. Figure 4.13 shows XRD pattern of 3 mol % (Y_2O_3+Al_2O_3): ZrO_2 sample sintered at 1200°C. Pure t-ZrO_2 was obtained in this sample. So, by addition of smaller amount of Al_2O_3 in 3mol%Y_2O_3 stabilized zirconia, pure t-ZrO_2 was formed.

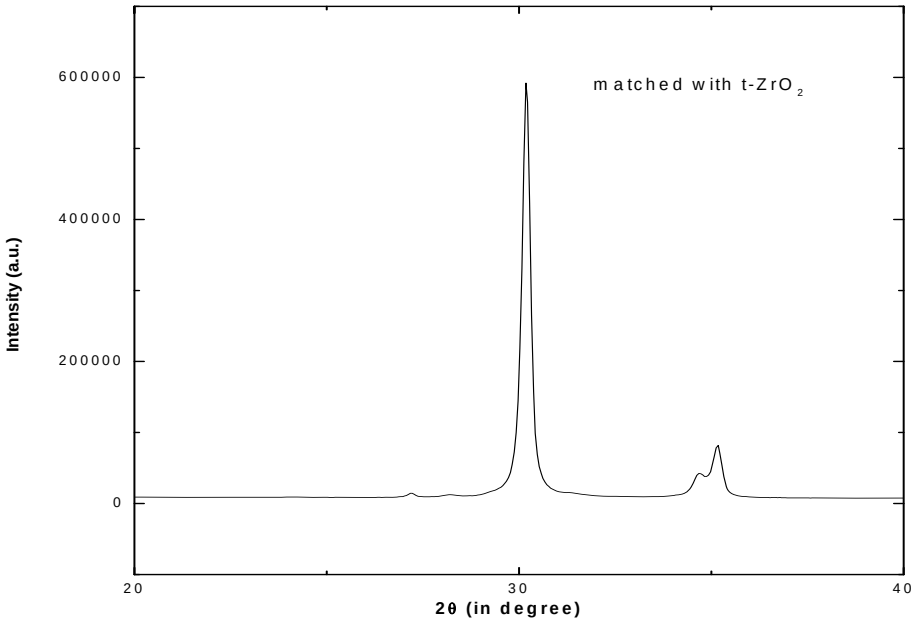

Fig. 4. 13: XRD pattern of sintered (1200°C) 0 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites

CHAPTER 5:

CONCLUSIONS AND FUTURE WORK

CONCLUSIONS

Major outcomes of this project work are:

- 3 mol % (Y_2O_3): ZrO_2, 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 and SiO_2 doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 have been successfully prepared using precipitation route using hydrazine hydrate as a precipitating agent.
- All these samples are sintered at different temperatures ranging from 1200°C to 1500°C in order to study the density and microstructure of these samples.
- It was found that SiO_2 doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites are showing better density and better microstructure than that of the parent sample (3 mol % (Y_2O_3 + Al_2O_3): ZrO_2).
- Phase segregation of secondary phase was observed for SiO_2 doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites sintered at 1300 °C.
- Maximum density and better microstructure was obtained for SiO_2 (0.05g and 0.1 g) doped 3 mol % (Y_2O_3 + Al_2O_3): ZrO_2 composites sintered at 1500°C.

FUTURE WORK

The parent samples can be co-doped further with different concentration of SiO_2 and detail study could provide a good densification in the microstructure with increase in their density and decrease in their porosity. The sintering temperature can be studied at a very high temperature of about 1650^0C or 1700^oC. All the samples can be characterized using different test based on mechanical point of view. Mechanical test such as hardness, fracture strength, young's modulus etc. could be done so that these composites could be useful for dental application.

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